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The Powder ESR Spectra of Some Bis(amino acidato)copper(II) Complexes

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Copper(II) complexes with some natural amino acids were prepared, and their powder ESR spectra were measured. The pattern types of the ESR spectra of these Cu(II) complexes with amino acids were classified into four types, and by the pattern type, the *cis*- or *trans*-isomer was estimated.

Many X-ray crystallographic investigations of bis(amino acidato)copper(II) complexes[1–12] have revealed that the amino acids are usually bidentately-coordinated to the metal through the nitrogen (N) of the amino group and the oxygen (O) of the carboxyl group. Though there is the possibility of a *cis*- or *trans*-coordination for a bis-complex, the bis(glycinato)copper(II) monohydrate reported by Tomita[13] was the first example of the *cis*-configuration. Since then other *cis*-complexes have been found[4,5,8,10] and many bis(amino acidato)copper(II) complexes have been investigated by X-ray crystallography,[1–12] infrared spectra,[14,15] visible diffuse reflectance spectra,[16] and ESR.[17–20]

In this paper, the powder ESR spectra of these complexes will be presented and discussed.

Experimental

Materials. The copper(II) complexes used in this study were as follows: $Cu(gly)_2\cdot H_2O$-(I), $Cu(gly)_2\cdot H_2O$-(II), $Cu(L\text{-}val)_2$, $Cu(DL\text{-}val)_2\cdot H_2O$, $Cu(L\text{-}ile)_2\cdot H_2O$, $Cu(DL\text{-}ile)_2\cdot H_2O$, $Cu(L\text{-}asn)_2$, $Cu(L\text{-}arg)_2(NO_3)_2\cdot 3H_2O$, $Cu(L\text{-}trp)_2$, $Cu(L\text{-}gln)_2$, $Cu(L\text{-}ala)_2$, $Cu(DL\text{-}ala)_2$, $Cu(L\text{-}ser)_2$, $Cu(L\text{-}thr)_2\cdot H_2O$, $Cu(DL\text{-}phe)_2$-(I), $Cu(DL\text{-}phe)_2$-(II), $Cu(L\text{-}phe)_2$, and $Cu(L\text{-}leu)_2$, where the abbreviations used are gly : glycine, val : valine, ile : isoleucine, asn : asparagine, arg : arginine, trp : tryptophane, gln : glutamine, ala : alanine, ser : serine, thr : threonine, phe : phenylalanine, and leu : leucine.

Preparation. The $Cu(gly)_2\cdot H_2O$-(I) and $Cu(gly)_2\cdot H_2O$-(II) were prepared by the method of Tomita[13]; the $Cu(L\text{-}val)_2$, $Cu(L\text{-}ile)_2\cdot H_2O$, and $Cu(L\text{-}gln)_2$, by the method of Neuberg *et al.*[21] from basic $Cu(OH)_2\cdot CuCO_3$, and the $Cu(DL\text{-}val)_2\cdot H_2O$, $Cu(DL\text{-}ile)_2\cdot H_2O$, $Cu(L\text{-}asn)_2$, $Cu(L\text{-}trp)_2$, $Cu(L\text{-}ala)_2$, $Cu(DL\text{-}ala)_2$, $Cu(L\text{-}phe)_2$, and $Cu(L\text{-}leu)_2$, by the method of Abderhalden and Schnitzler[22] from freshly-prepared $Cu(OH)_2$, while the $Cu(L\text{-}arg)_2(NO_3)_2\cdot 3H_2O$ was prepared by a method similar to that described by Dubois.[23] The $Cu(L\text{-}ser)_2$ was prepared by the methods of both van der Helm and Franks[4] and of Abderhalden and Schnitzler[22]; the two complexes thus obtained were identical. The $Cu(DL\text{-}phe)_2$-(I) and $Du(DL\text{-}phe)_2$-(II) were prepared by the method of Herlinger *et al.*[14] All the ligand molecules were commercially available.

Each molecular formula was determined by elementary analysis and was confirmed by studying the far-infrared spectrum.

Measurements. The ESR spectra (powdered samples) of the complexes were measured at room temperature with a JEOL X-band ESR spectrometer, model JES-ME-3X, equipped with a 100 KHz field modulation unit.

Results and Discussion

1) $Cu(gly)_2\cdot H_2O$-(I) and $Cu(gly)_2\cdot H_2O$-(II).

Tomita[13] suggested that bis(glycinato)copper(II) monohydrate was a *cis*- and that dihydrate was a *trans*-complex. However, Yasui and Shimura[16] reported that the *trans*-complex was also a monohydrate, and the same result was obtained in this work. The separation of *cis*- and *trans*-complexes was confirmed by the methods of X-ray analysis,[2] infrared spectrum,[14,15] and visible diffuse reflectance spectrum.[16]

The powder ESR spectra of $Cu(gly)_2\cdot H_2O$-(I) and $Cu(gly)_2\cdot H_2O$-(II), checked by means of the infrared spectra, are shown in Fig. 1. It can be seen from Fig. 1 that, while the spectrum of *cis*-$Cu(gly)_2\cdot H_2O$ is clearly axial in character, that of *trans*-$Cu(gly)_2\cdot H_2O$ shows a distortion from the usual axial pattern. It is reasonable to expect that the *trans*-complex would display such a rhombic distortion due to the difference in Cu–O and Cu–N bond lengths. The ESR spectrum of *trans*-$Cu(gly)_2\cdot H_2O$ was measured for the first time.

2) The Other Bis(amino acidato)copper(II) Complexes.

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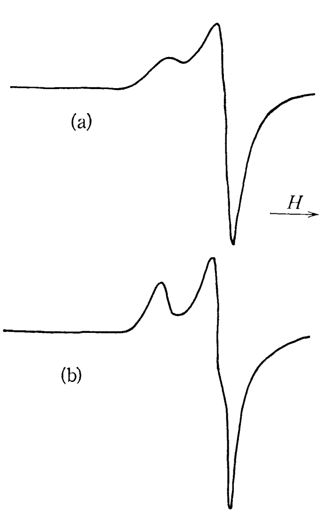

Fig. 1. The powder ESR spectra of *cis*-Cu(gly)$_2$·H$_2$O-(I) (a) and *trans*-Cu(gly)$_2$·H$_2$O-(II) (b).

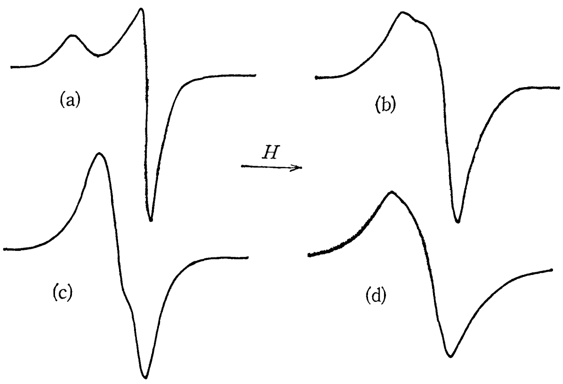

Fig. 2. The different types of the powder ESR spectra.
(a) Cu(L-val)$_2$-type, (b) Cu(L-trp)$_2$-type
(c) Cu(L-thr)$_2$·H$_2$O-type, (d) Cu(L-ala)$_2$-type

Figure 2 shows four typical polycrystalline ESR spectra of bis(amino acidato)copper(II) complexes: (a) Cu(L-val)$_2$, (b) Cu(L-trp)$_2$, (c) Cu(L-thr)$_2$·H$_2$O, and (d) Cu(L-ala)$_2$. Cu(L-val)$_2$, Cu(L-ile)$_2$·H$_2$O, Cu(DL-ile)$_2$·H$_2$O, Cu(L-asn)$_2$, Cu(L-arg)$_2$(NO$_3$)$_2$·3H$_2$O, and Cu(DL-phe)$_2$-(II) belong to the Cu(L-val)$_2$-type; Cu(L-trp)$_2$, Cu(DL-ala)$_2$, Cu(L-gln)$_2$, and Cu(DL-val)$_2$·H$_2$O belong to the Cu(L-trp)$_2$-type, and Cu(L-thr)$_2$·H$_2$O and Cu(L-ser)$_2$ belong to the Cu(L-thr)$_2$·H$_2$O-type, while Cu(L-ala)$_2$, Cu(DL-phe)$_2$-(I), Cu(L-phe)$_2$, and Cu(L-leu)$_2$ belong to the Cu(L-ala)$_2$-type.

The *cis*- and *trans*-complexes determined or estimated in this and other studies[2–5,12,14,16] are summarized in Table 1. The column for the ESR spectra in Table 1 shows the type of the powder ESR spectrum. Figure 2 shows that Cu(L-val)$_2$ gives an axial pattern, while Cu(L-trp)$_2$, Cu(L-thr)$_2$·H$_2$O, and Cu(L-ala)$_2$ give a non-axial pattern (clearly neither rhombic nor isotropic). From Table 1, the complexes of the Cu(L-val)$_2$-type can be found to be all *cis*-complexes except for the result of infrared spectra of Cu(L-val)$_2$.[14] On the other hand, the complexes of the Cu(L-trp)$_2$-type, the Cu(L-thr)$_2$·H$_2$O-type, and the Cu(L-ala)$_2$-type are all found to be *trans*-complexes except for the results of the X-ray analysis of Cu(L-ser)$_2$.[4] Therefore, the complexes of the Cu(L-val)$_2$-type are estimated to be *cis*-complexes, and the complexes of the Cu(L-trp)$_2$-type and the Cu(L-ala)$_2$-type, *trans*-complexes.

Although there is a difference between the results on Cu(L-val)$_2$ by Herlinger *et al.*[14] and those by Yasui and Shimura,[16] it may be believed to be a *cis*-complex on the basis of the above discussion.

According to van der Helm and Franks, Cu(L-ser)$_2$ forms a square pyramidal complex.[4] The four atoms (N$_A$, N$_B$, O$_{1A}$, O$_{1B}$) are not coplanar, but form a very flattened tetrahedron.[4] This is a complex with a lower symmetry than the other, so it may be supposed that this complex shows a non-axial pattern of the powder ESR spectrum. Only a coplanar *cis*-complex shows an axial pattern, while a non-coplanar *cis*-complex shows a non-axial pattern. Cu(L-thr)$_2$·H$_2$O is found to be the same type.

Bis(DL-phenylalaninato)copper(II) is a complex[14] which has *cis*- and *trans*-isomers, just as bis(glycinato)-copper(II)[13] and bis(L-alaninato)copper(II).[3,8] Cu(DL-phe)$_2$-(I) belongs to the Cu(L-ala)$_2$-type, and Cu(DL-phe)$_2$-(II) belongs to the Cu(L-val)$_2$-type; the

Table 1. Bis (amino acidato) copper (II) complexes determined or estimated by authors and other investigators

	Crystal structure	Infrared spectra[14]	Reflection spectra[16]	ESR spectra
Cu(gly)$_2$·H$_2$O-(I)	*cis*[2]	*cis*	*cis*	(*cis*)
Cu(gly)$_2$·H$_2$O-(II)	—	*trans*	*trans*	(*trans*)
Cu(L-ala)$_2$	*trans*[3]	*trans*	*trans*	L-ala (*trans*)
Cu(L-ser)$_2$	*cis*[4]	—	—	L-thr
Cu(L-ile)$_2$·H$_2$O	*cis*[5]	*cis*	*cis*	L-val (*cis*)
Cu(L-val)$_2$	—	*trans*	*cis*	L-val (*cis*)
Cu(DL-ile)$_2$·H$_2$O	—	*cis*	*cis*	L-val (*cis*)
Cu(DL-phe)$_2$-(II)	—	*cis*	—	L-val (*cis*)
Cu(DL-phe)$_2$-(I)	—	*trans*	—	L-ala (*trans*)
Cu(DL-ala)$_2$	—	*trans*	*trans*	L-trp (*trans*)
Cu(DL-val)$_2$·H$_2$O	—	*trans*	*trans*	L-trp (*trans*)
Cu(L-thr)$_2$·H$_2$O	—	—	*trans*	L-thr
Cu(L-phe)$_2$	*trans*[12]	*trans*	—	L-ala (*trans*)
Cu(L-leu)$_2$	—	*trans*	—	L-ala (*trans*)

former is found to be a *trans*-complex, and the latter, a *cis*-complex, from the results of the powder ESR spectra. These facts agree with those of the other infrared spectral study.[14] Thus, it supports our findings that a *cis*-complex or *trans*-complex found not only for bis(glycinato)copper(II), but also for bis(DL-phenylalaninato)copper(II), could be estimated by ESR. Table 1 shows the good agreement of our study with other studies.[2,3,5,12,14,16]

The geometrical isomers are believed to be classifiable as follows:

$\mathrm{Cu(gly)_2\cdot H_2O}$-(I)	*cis*
$\mathrm{Cu(gly)_2\cdot H_2O}$-(II)	*trans*
Cu(L-val)$_2$	*cis*
Cu(DL-val)$_2\cdot$H$_2$O	*trans*
Cu(L-ile)$_2\cdot$H$_2$O	*cis*
Cu(DL-ile)$_2\cdot$H$_2$O	*cis*
Cu(DL-phe)$_2$-(I)	*trans*
Cu(DL-phe)$_2$-(II)	*cis*
Cu(L-asn)$_2$	*cis*
Cu(L-arg)$_2$(NO$_3$)$_2\cdot$3H$_2$O	*cis*
Cu(L-trp)$_2$	*trans*
Cu(L-gln)$_2$	*trans*
Cu(L-ala)$_2$	*trans*
Cu(L-phe)$_2$	*trans*
Cu(L-leu)$_2$	*trans*

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